Laboratory Name: Los Alamos National Laboratory
B&R Code: KC0201020

FWP and/or possible subtask under FWP:
Radiation Damage Effects In Ceramics And Non-Metals

FWP Number: SCPE429

Program Scope: The goal of this program is to understand the radiation damage response of ceramics exposed to neutrons, ions or other energetic particles. Our studies of the damage response of ceramics address two objectives: (1) to predict microstructural evolution in ceramics exposed to radiation; and (2) to identify the physical aspects of ceramics that are effective in promoting radiation resistance. Our ultimate goal is to design new radiation resistant ceramics. We conduct particle irradiation tests on ceramics to evaluate their irradiation damage response. We also perform computer simulations of damage evolution in ceramics to assist in our understanding of radiation damage phenomena in these materials. Our research is focused on highly radiation-resistant ceramics.

Major Program Achievements (over duration of support): Using atomistic computer simulation techniques along with ion beam irradiation experiments on selected oxides, we have demonstrated that certain compounds with crystal structures similar to that of the mineral fluorite are highly resistant to displacive radiation damage. This radiation damage tolerance is very dependent on compound chemistry. For instance, our findings suggest that a large number of isochemical $A_2B_2O_7$ compounds with a structure called pyrochlore (very similar to the fluorite structure, but more highly ordered) should not exhibit resistance to radiation damage, while other $A_2B_2O_7$ compounds should be highly radiation tolerant. The radiation tolerant $A_2B_2O_7$ compounds with the fluorite structure should be suitable hosts for actinide species (Th, U, Pu, etc.). This research has been published in Science: K. E. Sickafus, L. Minervini, R. W. Grimes, J. A. Valdez, M. Ishimaru, F. Li, K. J. McClellan and T. Hartmann, "Radiation tolerance of complex oxides," Science **289** (2000) 748-751. Most recently, we have combined density functional theory, molecular dynamics, and temperature accelerated dynamics, to demonstrate how irradiation-induced defects evolve over long timescales (the oxides MgO and $MgAl_2O_4$ were chosen as a model oxides for calculation purposes). This work was recently published in Physical Review Letters: B. P. Uberuaga, R. Smith, A. R. Cleave, F. Montalenti, G. Henkelman, R. W. Grimes, A. F. Voter and K. E. Sickafus, "Structure and mobility of defects formed from collision cascades in MgO," Phys. Rev. Lett. **92 (11)** (2004) 5505.

Program Impact: Early work on this program laid the foundation for our current understanding of the behavior of model ceramic oxides (such as periclase (MgO) and corundum (Al_2O_3)) in a radiation damage environment. Recent developments on this program have led to an exciting new predictive capability to predict radiation damage evolution in model oxides such as MgO to time scales approaching experimental (order of seconds). Other efforts: Kurt Sickafus organized an international symposium on "Spinel Compounds: Structure Property Relations" at the Annual Meeting of the American Ceramic Society, Cincinatti, OH (1998). The proceedings was published as a special topical issue of the Journal of the American Ceramic Society (Vol. 82(12) 1999). Kurt Sickafus served as Director of a NATO-ASI international school entitled "Radiation Effects in Solids," held in Erice, Sicily in July, 2004. Kurt served as chair the 13^{th} International Conference on Radiation Effects in Insulators, held in Santa Fe, NM, Aug. 28 - Sept. 02, 2005. Kurt Sickafus and Blas Uberuaga served as Guest Editors (NIM-B) for the proceedings of this conference. Blas is co-organizer of a symposium entitled "Materials Innovations for Next-Generation Nuclear Energy," to be held at the MRS Fall 2007 meeting in Boston, MA.

Interactions: R. W. Grimes (Imperial College); R. Smith (Loughborough University); M. Ishimaru (Osaka University); K. Yasuda (Kyushu University); Simon Phillpot (U. Florida); V. T. Gritsyna (Kharkiv State University, Kharkiv, UKRAINE). *Internal LANL Interactions*: Art Voter, Steve Valone, Marius Stan, Chris Stanek, Cynthia Reichhardt, and Mike Baskes.

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):
Fellow of the American Ceramic Society to Frank Clinard (1986)
Foreign Distinguished Visiting Scientist at JAERI, Tokai, JAPAN to Frank Clinard (1987)
Los Alamos National Laboratory Fellow's Prize to Mike Nastasi (1995)
Fellow of the American Ceramic Society to Kurt Sickafus (1998)
Fellow of Los Alamos National Laboratory to Mike Nastasi (2000)
Los Alamos National Laboratory Fellow's Prize to Kurt Sickafus (2001)
2002 OBES Chunky Bullet competition co-winner (2002)

Personnel Commitments for FY2006 to Nearest +/-10%:
K. Sickafus (100%), J. Valdez (100%), B. Uberuaga (50%).

Authorized Budget (BA) for FY04, FY05, FY2006:
FY04 BA $ 843,000 **FY05 BA $** 809,000 **FY06 BA $** 1,026,000

Laboratory Name: Los Alamos National Laboratory
B&R Code: KC0201020

FWP and possible subtask under FWP:
Deformation Physics of Ultrafine Scale Materials

FWP Number: SCPE486

Program Scope: This program investigates the unusual deformation physics being discovered in ultrafine scale materials that lead to strength levels near the theoretical limit of strength for perfect crystals. The program involves a synergistic combination of atomistic simulations and experimental methods. Current focus is primarily on nanolayered metallic composites. The integrated approach consists of synthesis by vapor deposition; structure-property correlations by means of transmission electron microscopy, x-ray diffraction, microtensile and nanoindentation testing; and atomistic simulations of deformation behavior.

Major Program Achievements (program started in FY00, with full funding in FY01)**:**
Nanoscale design of metals with strengths approaching the theoretical limit: An increase of up to two orders of magnitude in strength over bulk materials is observed when the structural scale of the nanolayered composites is reduced to 1-2 nanometers.
New Strengthening Mechanisms in Nanolayered Materials: Atomistic modeling reveals a new strengthening mechanism in incoherent interfaces; an unusually high resistance to slip transmission originates from dislocation-induced shear of 'weak' interfaces and concomitant dislocation core spreading within the interfaces. We find that coherent multilayers derive their high strengths primarily from coherency stresses.
High strength and high radiation damage tolerance: We discovered that interfaces that act as obstacles to slip also are also excellent sinks for radiation-induced defects. Thus, the nanolayered composites exhibit a combination of high-strength and high radiation-damage tolerance.

Program impact: This program has discovered new regimes of plasticity in nanoscale composite materials that have led to new scientific models that help to understand the origins of mechanical behavior of nanoscale materials as their strength approaches theoretical limits. The work from this program is largely the basis for the nanomechanics thrust area in the upcoming Center for Integrated NanoTechnologies in New Mexico. The discovery of high radiation damage tolerance will significantly impact the design of structural materials for future nuclear reactors.

Interactions (FY'06):
Hussein M. Zbib (Washington State University), Peter M. Anderson (Ohio State University), Amiya K. Mukherjee (UC, Davis), Ian M. Robertson (University of Illinois), Tamas Ungar (Eotvos University Budapest, Hungary).

Recognitions, Honors and Awards (since FY'00):
R.G. Hoagland, LANL, Matthias scholar at LANL, FY'00.
P.M. Anderson, Ohio State University, Matthias scholar at LANL, FY'02.
J.D. Embury, 2005 ASM Edward DeMille Campbell Memorial Lecture.
F. Spaepen, 1999 Humboldt Research Award for Senior U.S. Scientists.
F. Spaepen, 2002 Robert Franklin Mehl Award, The Minerals, Metals & Materials Society (TMS).

65 refereed publications, including 3 book chapters; over 30 invited talks at national/ international symposia.
9 symposia organized (MRS Fall 2000; United Engineering Foundation, Italy, 2001; TMS Annual 2003; MRS Spring 2003; TMS Annual 2005; MRS Spring 2004; MRS Spring 2005; MRS Spring 2006, MRS Fall 2006). Edited 2 journal special issues: Scripta Materialia issue titled *Deformation and Stability of Nanoscale Metallic Multilayers* (March 2004), and MRS Bulletin issue titled *Mechanical Properties of Nanostructured Materials*, 1999.

Personnel Commitments for FY2006 to Nearest +/- 10%:
R.G. Hoagland (LANL, 30%), A. Misra (LANL, 30%), F. Spaepen, (Harvard University, 5%), J.D. Embury (LANL-Affiliate, 10%), J. P. Hirth (LANL-Affiliate, 10%), S.G. Srinivasan (LANL TSM, 20%), A. Donohue (100%, GRA, Harvard University), F. E. Akasheh (100%, GRA, Washington State University), K. Hattar (summer GRA), Y.C. Wang (LANL PD, 50%), Jian Wang (hired September 2006).

Authorized Budget (BA) for FY04, FY05, FY06:
FY04 BA $759,000 **FY05 BA** $729,000 **FY06 BA** $814,000

Laboratory Name: Los Alamos National Laboratory
B&R Code: KC0201020

FWP and possible subtask under FWP:
Multi-scale Study of the Role of Microstructure in the Deformation Behavior of Hexagonal Materials

FWP Number: SCPE401

Program Scope: Our primary goal is to use an integrated experimental and theoretical approach to characterize the complex role played by dislocations, twins, and grain boundaries during plastic deformation. The scope of the proposed work is to connect the various length scales and physical mechanisms governing deformation (micro, meso and macro scale), in order to explain the overall mechanical response of metallic aggregates. The focus of this program is hexagonal materials, where the coupling between the microscopic mechanisms and the macroscopically observed response is very strong, and not completely understood. The paradigm of this program is to reveal such coupling by studying complex testing histories involving changes in strain path and/or temperature and/or strain rate

Major Program Achievements (over duration of support): This program uses as a starting point the developments achieved under the previous Mechanical Properties Program. We use polycrystal constitutive laws as a platform for implementing microstructure models and relate them to macroscopic plastic response and anisotropy, for a wide range of strain, temperature and strain-rate regimes.
We have incorporated experimental information about the grain microstructure and its evolution into our polycrystal models. Specifically, we have developed experiment-based models for dislocation walls, intragranular banding, misorientation, and twin domains. We have applied this integrated approach to hexagonal materials, with emphasis in Zr and Mg, but also to Be, Ti and Hf. We are making intensive use of in-house neutron diffraction facilities for characterizing microstructure, we started using the Advanced Photon Source (Argonne) for the same purpose, and we have developed new automated or combined techniques for performing TEM and OIM analysis. We have developed new Multiple-State Embedded Atom Potentials for a basic understanding of dislocation-twin interactions. And we have developed physically-based polycrystal constitutive models for describing the mechanical response of HCP aggregates.

Program impact: The effort on texture, anisotropy, constitutive description and modeling of polycrystal plasticity come at a time when the Materials Science community started becoming aware of these issues. It changed the way in which constitutive modeling was approached by the scientific community, and Los Alamos is regarded as leading the field in such issues. Today the field has matured, and the scientific community is looking at the specific role played by defects such as dislocations, grain boundaries and twins on the overall mechanical response of polycrystals. Such quest, which can only be answered through a basic and integrated study of such features, is the general scope of this program. We predict that our specific focus on hexagonal aggregates, such as Zr and Be alloys, will have a direct impact on basic material science and in Los Alamos research programs. In addition, the study of Ti and Mg alloys will impact energy related technologies. As a spin-off, we foresee an impact in the understanding of systems where phase transformations are important, such as piezo-electric and shape-memory alloys.

Interactions: A. J. Beaudoin (U of IL-Urbana), I. Robertson (U. of IL-Urbana), D. Embury (McMaster U.), S. I. Wright (TexSEM Labs), J.P. Hirth (LANL consultant), S.R. Agnew (U. of Virginia), S. Kalidindi (Drexel U.), W. Horstemeyer (MS State U.), P. van Hove (Law. Berk. NL), C.P Wong (GA Inst. Tech.), R. Holt (Queen's U.), I. Karaman (Texas A&M U.), R. Asta (Northwestern U.)

Recognitions, Honors and Awards (at least partly attributable to support under this FWP): U. Fred Kocks, Fellow, (NAE, TMS, LANL, ASM, APS, AIME); T.E. Mitchell, Fellow (LANL, TMS, ASM, APS, ACS), Honorary D. Sc., U. of Cambridge; Symp. and special issue of Phil. Mag. A in his honor; M.I. Baskes, Fellow (TMS, LANL, IP), DOE BES Award for Sustained Outstanding Research, Journal Editor, *Modeling and Sim. in Materials Sci. and Eng.*; About 30 Invited Presentations (altogether in the last three years) related to this project. About 30 papers published in International peer reviewed journals in the last three years related to this project.

Personnel Commitments for FY06 to Nearest +/- 10%: C. Tomé (PI, 50%), M. Baskes (15%), I. Beyerlein (40%), G Kaschner (30%), A Misra (20%), S. Srivilliputhur (30%), R. McCabe (25%), E. Cerreta (20%), B. Clausen (30%), G. Proust (100%, post-doc), D. Battacharya (50%, post-doc), A. Jain (100%, PhD student).

Authorized Budget (BA) for FY04, FY05, FY06:
FY04 BA $ 1,043,000 **FY05 BA $ 1,001,000** **FY06 BA $ 981,000**

Laboratory Name: Los Alamos National Laboratory
B&R Code: KC0201020

FWP and possible subtask under FWP:
Nanophosphors: Fundamental Science of Insulators in the Nanoscale Regime

FWP Number:
SCPE972

Program Scope: Fabrication and characterization of nanoscale, inorganic, insulating phosphors (nanophosphors) to assess the role of reduced dimensionality on their optical and magnetic resonance properties. Owing to their unique optical and magnetic properties, rare-earth ions are employed as dopant ions in nanophosphors to probe the atomic environment; for example, crystalline electric field, spin-orbit coupling, phonon density-of-states, Zeeman interaction, and nuclear hyperfine interaction. Utilizing optical and electron paramagnetic resonance techniques in tandem provides detailed information on the effects of reduced dimensionality. Results of this work are expected to yield new nanotechnology materials.

Major Program Achievements (over duration of support): Nanophosphor Y_2SiO_5:Ce (*n*-YSO), Lu_2SiO_5:Ce (*n*-LSO), Y_2O_3:Tb (*n*-YO), and LaF_3:Ce (*n*-LF) were prepared by solution-combustion synthesis and wet chemistry methods yielding nanophosphor crystallite sizes ranging from sub-10 nm to *ca.* 50 nm. Dopant concentrations were varied over a broad range for each the nanophosphors and concentration quenching curves were measured. *n*-YSO exhibits concentration quenching at 1 at% and 4 at% under uv and x-ray excitation, respectively, which is considerably higher than possible in bulk phosphors. Differences in the quenching curves are due to the method of excitation. Photoluminescence excites only the dopant levels whereas x-rays produce excitons that may decay via other relaxation processes therby affecting light yield. Temperature and concentration dependent lifetimes for *n*-YSO can be explained by a model that considers excitation and energy transfer via dopant ions. An important component of this model is phonon density of states. Because nanophosphors are disordered, the dopant ions have a distribution of energies around a mean. For those energy levels that are slightly higher than the mean, it is necessary to invoke phonon relaxation for energy transfer to occur. Reduced dimensionality cuts off the low energy phonon modes and alters the relaxation process.

Installation of a He cryostat into the electron paramagnetic resonance (EPR) spectrometer allowed detection of the Ce ions in *n*-YSO and *n*-LSO. Comparison of EPR spectra for bulk and *n*-YSO (LSO) shows significant shifts in the *g*-values as well as broadening of the line width relative to bulk. These results are consistent with the change in oxygen coordination of *n*-YSO (7 & 9 oxygen coordination) and bulk YSO (6 & 7 oxygen coordination). The line broadening in *n*-YSO is indicative of oxygen sublattice disorder.

A major achievement of the recent EPR work is the observation of F^+ centers (electron trapped at oxygen vacancy) in bulk and *n*-YSO (LSO). For several years it has been speculated that the major defect in these materials is electrons trapped at oxygen vacancies, which lead to afterglow. Heretofore no experimental evidence could confirm this hypothesis. We identified the EPR signal of this defect and showed that it could be manipulated via radiation and annealing. Moreover, we demonstrated that *n*-YSO (LSO) contains fewer of these defects than bulk YSO and, consequently, exhibits much weaker afterglow.

Program impact: Results provide new insights into the role of reduced dimensionality on nanophosphor behavior, and guides development of new nanomateials. Especially exciting is the fundamental information derived from the EPR studies, which is a technique that is not being widely pursued in nanophosphors, but, as we have shown, offers tremendous potential.

Interactions:J.-Y. Kim and K. S. Hong (Seoul National University); L. Clark and J. Williams (Reuter-Stokes); Steve Duclos (GE Global Research); Peter Rez (Arizona State). Internal LANL Interactions: K. Ott, E. McKigney, K. Sickafus, J. Valdez, B. Uberuaga, D. Smith, M. Graf, S. Conradson, Y. Wang.

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):
R. E. Muenchausen, D. W. Cooke, J.-K. Lee, M. Nastasi and Q. Jia, “Method for Preparation of Rare-Earth Oxyorthosilicate Phosphor Films.” S-104,811 (patent pending). J. Smith & B. Bennett (LAAP Award).

Personnel Commitments for FY2006 to Nearest +/- 10%: W. Cooke (35%); R. Muenchausen (10%); B. Bennett (35%); J. Smith (30%);); L. Jacobsohn (10%).

Authorized Budget (BA) for FY04, FY05, FY06:
FY04 BA $ 0 **FY05 BA $** 450,000 **FY06 BA $** 441,000

Laboratory Name: LANL
B&R Code: KC02 01030

FWP and possible subtask under FWP:
Electronic Processes in Solid State Organic Electronic Materials
FWP Number:
SCPE973

Program Scope:

Organic electronic materials are condensed phases of p-conjugated molecules and intermolecular interactions are critical in determining the condensed phase properties. The electronic properties of the dense films are not the same as those of the isolated molecules or single polymer chains. A major theme of this proposed research is to determine which features of the electronic structure of the isolated molecules are maintained and which are modified in the condensed phase and to use our understanding of molecular electronic structure to describe the behavior of the condensed phases. The goal of the project is to provide an understanding of the fundamental physical processes that are important in determining the properties of organic electronic materials. Physical processes of particular interest include: electrical injection, charge transport, electron spin injection, transport and dynamics and exciton dynamics and transport.

Major Program Achievements (over duration of support):

Organic Spin Physics - Measured spin dependent optical properties of a series of metal-organic compounds. Developed a model based on spin orbit splitting from the heavy metal atoms to describe the experimental results.

Electronic Structure of Condensed Phases of Organic Molecules - Utilized molecular dynamics calculations to determine solid state molecular configurations. These molecular configurations were used as input to large scale quantum mechanical electronic structure calculations. The calculated electronic structure explains systematics observed in the transport properties of organic semiconductors.

Charge Transport in Composite Organic Semiconductors - Measured charge transport in isoelectronically doped organic semiconductors using time-of-flight transient photoconductivity and current-voltage characteristics of unipolar and bipolar test structures. Observed novel electric field dependent charge transport in these composite materials.

Organic Semiconductor Device Models - Developed the first device model for the light-emitting field effect transistor, recently invented at UC Santa Barbara and University of Cambridge. The model quantitatively describes the observed device properties.

Program impact:
Our integrated theoretical and experimental approach has demonstrated the important role of: spin orbit coupling in metal-organic systems; structural disorder in determining electrical transport properties of organic semiconductors; isoelectronic dopant energy levels in composite system charge transport; and carrier trapping at interfaces in organic field effect transistors.

Interactions:
Internal- National High Magnetic Field Laboratory (S. Crooker), Center for Integrated Nanotechnology (S. T. Picraux, A. Balatsky, S. Tretiak), Los Alamos Neutron Science Center (M. Fitzsimmons)
External-University of Cambridge (P. Littlewood, R.H. Friend, H. Sirringhaus, N. Greenham), UC Santa Barbara (A.J. Heeger, G. Bazan), U Minnesota (P. Ruden), Johns Hopkins U (H. Katz), U Florida (F. So)\

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):
Co-Chair of Spring MRS Meeting on Solid State Lighting (B. Crone); Panel Member of BES Solar Workshop (D. Smith); Panel Member (B. Crone) and Session Co-Chair (D. Smith) of BES Solid State Lighting Workshop; Advisory Board of the Workshop on Spintronic Effects in Organic Semiconductors, Bologna 2007 (D. Smith); Organizing Committee 1st Topical Meeting on Spins in Organic Semiconductors, Salt Lake City 2008 (D. Smith).

Personnel Commitments for FY2006 to Nearest +/- 10%:
Ian Campbell: 20%; Brian Crone: 20%; Richard Martin: 20%; Darryl Smith: 30%

Authorized Budget (BA) for FY04, FY05, FY06:
FY04 BA $ 0 **FY05 BA $ 450,000** **FY06 BA $ 441,000**

Los Alamos National Laboratory
B&R Code: KC0201050

FWP and/or subtask Title under FWP:
Ion-Enhanced Synthesis of Materials
FWP Number:
SCPE407
Program Scope: To develop a fundamental understanding of ion processed materials and to determine how ion processing parameters influence the material structure and functional properties. Experiments, theory and modeling are used to understand the underlying physics and fundamental processes responsible for the enhanced properties derived by materials synthesis by these methods.

Major Program Achievements (over duration of support): We have successfully developed the Plasma Immersion Ion Process (PIIP) to synthesis diamond-like-carbon (DLC) field emitters. Modeling showed that electron emission is dependent sp^3 contents and the aspect ratio of the emitting area. PIIP was then used to alter the surface topology and ratio of sp^2 to sp^3 carbon bonding at the surface and thereby control the electron emission behavior.

We have shown that the intrinsic stress in thin films form by ion assisted deposition techniques are strongly influence by the presence of grain boundaries, vacancies, interstitials and dislocations. An atomic interaction model has been developed to explain the source of intrinsic stress in thin films.

We have shown for the first time that the stress generated by radiation defects produced during the ion implantation of hydrogen into silicon promotes the formation of hydrogen-planner defects. The stress and resultant strain facilitate the nucleation and growth of hydrogen platelets on planes normal to the ion implantation direction.

We have shown that stresses grown into single crystal Si substrate via buried SiGe stain layers getter hydrogen in the same way that radiation damage derived stresses do. The concentration of H at the strain layer increases with increasing strain and for layers with very high strain and hydrogen concentrations, controlled cleave along the Si-SiGe interface occurs.

Program impact: Provides fundamental insight at the microscopic and atomistic levels on how ion-solid interactions enhance the properties and functionality of materials. This work has enabled the synthesis of novel and improved materials.

Interactions:, J. Mayer (ASU), S. S. Lau (UCSD), P. Chu (City U, Hong Kong), D. Lucca (Oklahoma State); *Internal LANL*: R. Hoagland, A. Misra, M. Baskes, J.G. Swadener, Q. Jia, J.K. Lee, L.G. Jacobsohn, D.W. Cooke

Recognitions, Honors and Awards: M. Nastasi: Fellow of LANL (2000), Recipient LANL Fellows Prize (1995), R&D 100 Award (1997), Exec. Officer of The Bohmische Physical Society (1997-), Edit. Board of Nuclear Instruments and Methods in Physics Research, Section B: (1997-), Principal Ed. J. of Materials Research (1997-2000), Chair MRS Bull Pubs Subcommittee (1994-1999), Member of International Meeting Committees: Ion Beam Modification of Materials (1995-), Chair of the Editorial Board of MRS Bull (1996-1999), *Adjunct Professor*, Univ. of Colorado, Arizona State Univ., Univ. of Maryland. Contributions over the life of the program (1996 – present): ~ 240 papers; 3 books and 5 edited volumes; 5 patents awarded; 4 PhDs awarded;

Personnel Commitments for FY2006 to Nearest +/- 10%: M. Nastasi (PI) 50%, Y. Wang 20%, Lin Shao (postdoc) 40%

Authorized Budget (BA) for FY04, FY05, FY06:
FY04 BA $ 541,000 **FY05 BA $** 333,000 **FY06 BA $** 326,000

Laboratory Name: Los Alamos National Laboratory
B&R Code: KC0202010

FWP and possible subtask under FWP:
Complex Electronic Materials

FWP Number: SCPE355

Program Scope: Research focuses on developing a fundamental understanding of the physics of complex and collective states in electronic materials by discovering new materials that reveal essential new physics. A necessarily broad range of experimental techniques, often at extremes of low temperatures, high fields and high pressures, is used to probe static and dynamic spin, charge and lattice degrees-of-freedom and their interactions on multiple length and time scales. Particular attention is given to highly correlated f-electron materials and layered cuprates, often in single crystal form, as exemplary complex electronic materials.

Major Program Achievements (over duration of support): Established the study of heavy-fermion materials as a new field of condensed matter physics through discoveries of numerous examples of unconventional superconducting, magnetic and semiconducting states in new correlated f-electron systems; discovered unconventional superconductivity in $PuCoGa_5$ and in a new family of Ce_nMIn_{3n+2} (M=Co, Rh, Ir; n=1,2) materials; discovered high T_c superconductivity in rare-earth cuprates, providing the first indication for the importance of CuO_2 planes; pioneered the now widely accepted importance of intrinsic inhomogeneity in the spin, charge and lattice of cuprates, using neutron and NMR spectroscopies; in $CeCoIn_5$, discovered evidence for Fulde-Ferrell-Larkin-Ovchinnikov state, first predicted nearly 40 years ago, and for an unusual form of quantum criticality; discovered superconductivity in hole-doped diamond; discovered a field-induced line of magnetic quantum-critical points within the pressure-induced superconducting state of $CeRhIn_5$.

Program Impact: Program is recognized internationally for its leadership in creating new science through the discovery and study of new correlated electron materials.

Interactions: Z. Fisk (U. C. Davis), D. E. MacLaughlin (U.C. Riverside), B. Buchner (University Cologne), C. Retorri (UNICAMP), J. M. Lawrence (U.C. Irvine), M. Nicklas (Max-Planck Institute for the Chemical Physics of Solids), P. Oppeneer (Uppsala University), G. Lander (ITU, Karlsruhe), V. Sidorov (IHPP, Troitsk), L. Greene (University of Illinois), Q. Si (Rice University) among many others.

Recognitions, Honors and Awards (at least partially attributable to support under this FWP or subtask): Z. Fisk-National Academy of Science, American Academy of Arts and Sciences, E. O. Lawrence Prize, DOE Award for Sustained Outstanding Research in Solid State Physics, APS New Materials Prize, APS Fellow, APS Div. Condens. Matt. Phys. Executive Committee, APS Buckley Prize Committee, LANL Fellow, editorial boards of Physica B and Phys. Rev. Lett.; P. C. Hammel-APS Fellow, LANL Fellow, LANL Fellows' Prize, APS Executive Committee of Instrumentation and Measurement Science; R. H. Heffner-APS Fellow; R. Movshovich-APS Fellow, LANL Fellows' Prize ; R. Pynn-APS Fellow, AAAS Fellow; J. L. Sarrao-APS Fellow, LANL Fellow's Prize; J. L. Smith- E. O. Lawrence Prize, DOE Award for Sustained Outstanding Research in Solid State Physics, APS New Materials Prize, APS Fellow, LANL Fellow, editorial boards of J. Alloys and Compds. and Phil. Mag.; J. D. Thompson- APS Fellow, AAAS Fellow, APS Div. Condens. Matt. Phys. Executive Committee, DOE Award for Sustained Outstanding Research in Solid State Physics, ISI Highly Cited Physicist, LANL Fellow, LANL Fellows' Prize, Japanese Society for the Promotion of Science Fellow; collectively served on numerous International Conference Advisory Committees and review panels, and within past year presented over 25 invited talks at international conferences/workshops/universities.

Personnel Commitments for FY2005 to Nearest +/-10%: J. D. Thompson (15%), W. Bao (35%), N. Curro (20%), J. J. Joyce (20%), T. Durakiewicz (15%), R. Movshovich (20%), F. Ronning (15%); J. L. Sarrao (10%); two postdocs (75%)

Authorized Budget (BA) for FY04, FY05, FY06
FY04 BA $850,000 **FY05 BA** $880,000 **FY06 BA** $850,000

Laboratory Name: Los Alamos National Laboratory
B&R Code: KC0202010

FWP and possible subtask under FWP:
Photoelectron Spectroscopy of Transuranics, subtask on Complex Electronic Materials

FWP Number:
SCPE355

Program Scope:
The electronic structure of actinide elements and compounds is investigated via photoelectron spectroscopy using both a novel laser plasma light source (LPLS) which is tunable between 27eV and 140 eV photon energy, as well as synchrotron radiation experiments. The LPLS uses a continuous-flow mercury target and a high power Nd:YAG laser to provide a tunable source of photons for photoelectron spectroscopy over the ultraviolet and soft x-ray energy range, encompasses the 5f resonant photon energies and regions of maximum change and intensity in 5f electron cross-sections. Surfaces are prepared via laser ablation which is among the best methods for preparation of transuranic surfaces in PES measurements. Both α- and δ-Pu display a sharp density-of-states near the Fermi energy, indicative of narrow bands, but neither fits the usual heavy fermion picture. From the cross section dependence we deduce a substantial 6d admixture in these bands. Angle resolved synchrotron work on uranium compound single crystals reveals definite 5f-6d hybridized bands even for cases of ordered magnetic moments. It now appears that the correct description of 5f-electron materials through Pu and its compounds is narrow band behavior very near the Fermi energy if the 5f electrons are not clearly localized in a magnetic configuration. In most cases including 4f systems, the f-electrons are confined to only part of reciprocal space. Photoemission measurements have now been made on single crystal U compounds (synchrotron), Np metal and compounds (NpAs, NpSb, NpTe - LPLS) and Pu metal and compounds ($PuIn_3$, $PuSb_2$, $PuCoGa_5$, $PuSn_3$, PuTe, PuSb, Pu_2RhGa_8 - LPLS). 2007 will see the first angle-resolved photoemission (ARPES) measurements on Pu materials with LANL having the only transuranic resonance photoemission (RESPES) or ARPES capabilities in the world.

Major Program Achievements (over duration of support):
With a unique experimental capability for transuranic materials, this program often provides essential information regarding transuranic electronic structure not available by other means. First spectroscopic identification of the dual nature of 5f electrons in Pu materials. First resonance photoemission data on Pu metal indicating hybridization of 5f levels with conduction states. Angle-resolved PES in 4f and 5f electron materials showing f-electron dispersion. Direct comparison between PES and calculations for α and δ-Pu. First measurement for Np compound 5f hybridization. LPLS design, development and construction as well as development of laser ablation for cleaning transuranics. Demonstration of itinerant magnetism in UTe. First photoemission of $PuCoGa_5$ demonstrating hybridization and the dual nature of the 5f levels.

Program impact:
Provides insight into the electronic structure of actinides and the fundamental nature of 5f electrons in Pu materials. The RESPES and ARPES capability for transuranics is unique in the world.

Interactions:
external collaborators include C.G. Olson (Ames Lab), H. Hochst (Univ. of Wisconsin), G. Lander (Karlsruhe), P. Riseborough (Temple), M. Jarrell (Univ. of Cincinnati), L. Havela (Charles University), M. Grioni (Lausanne), internal collaborators include David L. Clark (ADSMS), John Wills (T-1), Dave Moore (MST-16), L. Morales (MST-8), Jeff Hay (T-12), Rich Martin (T-12).

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):
Three members of this team won the Los Alamos Distinguished Performance Award in 1997 for work on the LPLS project, Joyce was also awarded the Los Alamos Achievement Award in 1996 and 2001 for work on the LPLS. Arko was named laboratory fellow in 2000 for his work on this project.

Personnel Commitments for FY2006 to Nearest +/- 10%:
J.J. Joyce 25% FTE
T. Durakiewicz 25% FTE
K.G.Graham 25% FTE

Authorized Budget (BA) for FY04, FY05, FY06:
FY04 BA $300,000 **FY05 BA $300,000** **FY06 BA $300,000**

Laboratory Name: LANL
B&R Code: KC020201

FWP and possible subtask under FWP:
Control over structure-property relationships of complex oxide films by designed strain, subtask on Complex Electronic Materials

FWP Number:
SCPE355

Program Scope:
Development and application of neutron and X-ray (synchrotron) scattering techniques to elucidate the influence of strain on magnetic phase coexistence and texture in complex oxide films. Specifically, we will determine the parameters of the strain and magnetic free energies (e.g., stiffness, anisotropy, exchange, atomic and magnetic structure etc.) as a function of applied stress. This information will be used to test the theory of magnetic phase coexistence and texture in complex materials developed by Ahn et al. and to adapt their theory to explicitly treat magnetism.

Major Program Achievements (over duration of support):
Capital equipment was acquired to upgrade our existing thin-film deposition system to deposit complex oxide films with large area (20 cm^2) suitable for neutron scattering. The equipment is being fabricated (we anticipate delivery January 2007). I conducted a search for a postdoctoral researcher (for this project), and have identified an ideal candidate. An offer is being formalized.

Program impact:
This project is a new project.

Interactions:
Discussed with **J. Budai (ORNL)** an opportunity to use microfocus synchrotron radiation to determine the atomic structures of ferromagnetic/conducting and antiferromagnetic/insulating phases in complex oxide films. Our intention is to undertake test measurements in the near future at the Advanced Photon Source.
Discussed with **J.K. Lee (LANL)** an opportunity to use ion implantation to bend substrates. This technique will allow us to apply a controlled tensile or compressive stress to the film (by bending its substrate). Lee successfully applied the technique to bend $SrTiO_3$—a candidate substrate for my study. I will characterize the strain of a few test samples in the near future.
Discussed with **T. Lookman (LANL)** his theory of strain and magnetic phase coexistence and texture in complex oxides. I understand what information Lookman requires, and how I will obtain this information with X-ray and neutron scattering.

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):
Fellow of the American Physical Society

Personnel Commitments for FY2006 to Nearest +/- 10%:
M.R. Fitzsimmons (30%)

Authorized Budget (BA) for FY04, FY05, FY06:
FY04 BA $ 0 **FY05 BA $** **0** **FY06 BA $** 150,000

Laboratory Name: Los Alamos National Laboratory
B&R Code: KC0202020

FWP and possible subtask under FWP:
Science of Electronic and Optical Interactions between Coupled Nanostructures
FWP Number: SCPE395

Program Scope: The goal of this project is the understanding of the behavior of interacting nanophotonic and nanoelectronic structures. One focus area is interactions that produce changes in the optical and electronic properties of the nanostructures, including the effect of inter-dot interactions on the optical and electronic properties of self-assembled and colloidal quantum dot arrays and the exploration of novel composite materials consisting of semiconductor colloidal quantum dots embedded in semiconductors. A second focus area is the study of nanoelectronic structures in photonic bandgap materials and photonic crystal fibers where the interplay between the restricted electronic and photonic density of states can produce large optical nonlinearities, inhibit radiative decay, and lead to high speed optical switching.

Major Program Achievements (over duration of support): We explored the effect of semiconductor nanaocrystal (NC) "geometry" on the rates of the multi-particle decay. In particular, we study the influence of the zero- to one-dimensional (1D) transformation on multi-particle Auger recombination using a series of elongated semiconductor NCs (quantum rods). We observe the transition from the three- to two-particle recombination process as the nanocrystal aspect ratio is increased. This transition implies that in the 1D confinement limit, Auger decay is dominated by Coulomb interactions between 1D excitons that recombine in a bimolecular fashion. We explored the use of NC core-shell heterostructures for suppressing Auger recombination. Specifically, we use inverted ZnSe(core)/CdSe(shell) nanoparticles to study the effect of type I vs. type II carrier localization on multiparticle Auger decay and optical gain performance of NCs. We observe that both Auger recombination rates and the amplified spontaneous emission thresholds are reduced in the case of type II localization. Furthermore, we use these hetero-NCs to demonstrate efficient amplified spontaneous emission that is tunable across a "difficult" range of green and blue colors.

We explored a novel approaches for injection of charges into semiconductor nanocrystals by using "noncontact" pumping mediated by high-efficiency energy transfer (ET) from a proximal quantum well (QW), using an *inverted* LED design, in which an InGaN QW was grown on top of a thick, p-doped GaN barrier using metal-organic chemical-vapor deposition. The structure was further capped with a thin, 3-nm, n-type GaN layer and electrical contacts were applied by plasma etching. In this way it was possible to take advantage of the much higher mobility of n-GaN compared to p-GaN and to obtain significant current spreading despite the small thickness of the n-type injection layer. The structure was completed with a monolayer of CdSe nanocrystals. The ratio between the nanocrystal and the QW emission intensities, which approximately determined the color conversion efficiency, was nearly 15%.

We have developed experimental tools for visualizing complex nonlinear optical processes in Photonic Crystal Fibers PCFs in both time and frequency simultaneously. Using the technique of Cross-Correlation Frequency-Resolved Optical Gating (XFROG) we studied ultrashort pulse dynamics in a multitude of silica glass, and more exotic material waveguiding structures. We discovered and explained the process of intermodally phase-matched harmonic generation in silica cobweb PCFs and the role of Raman solitons in multicolor emission. In small-core silica PCF we observed the complex dynamics of solitons in the vicinity of the second dispersion zero, specifically the soliton stabilization against Raman shift and generation of Cherenkov continuum across the zero dispersion point. For the first time we performed direct studies of scattering of continuous waves on solitons - a fundamental problem in nonlinear fiber optics. Two types of resonant scattering were experimentally identified and explained by the analytical theory and numerical modeling. Finally, a technologically important phenomenon of supercontinuum generation in the telecom wavelength region was studied using time-frequency visualization with XFROG and new understanding of the generation mechanisms are being identified based on this data.

Program impact: This project addresses important scientific issues at the forefront of nanoscience. It complements ongoing R&D activities ongoing at the Center for Integrated Nanotechnologies.

Interactions: Department of Physics, University of Bath, UK; Department of Physics, University of Florida, Gainesville; Department of Chemistry, MIT; Department of Physics, Georgia State University, Department of Physics, Tufts University

Recognitions, Honors and Awards: V.I. Klimov—Los Alamos Laboratory Fellow (2004); A.J. Taylor—Fellow of AAAS (2006); 21 invited talks since 2004; A.J. Taylor, Program Chair, OSA Nonlinear Optics Conference (2004), and Program Vice-Chair, GRC on Ultrafast Phenomena in Cooperative Systems (2008)

Personnel Commitments for FY2006: Staff: A. Efimov, 25%, V.I. Klimov, 5%; H. Htoon, 25%

Authorized Budget: FY04 BA $ 204,000 FY05 BA $190,000 FY06 BA $140,000

Laboratory Name: Los Alamos National Laboratory
B&R Code: KC020202

FWP and possible subtask under FWP:
Thermoacoustics for Hydrogen Production

FWP Number:
SCPE979

Program Scope:
We focus on hydrogen-specific issues of thermoacoustic mixture separation. We consider which chemical reactions are most suitable for hydrogen production using thermoacoustics, and investigate scientific issues such as inter-channel thermoacoustic streaming and long-channel power transduction that will be essential for use of thermoacoustics in this arena. We keep our general-purpose, publicly available thermoacoustics code DeltaE and its documentation aligned with the long-term vision of solar thermal hydrogen production.

Major Program Achievements (over duration of support):
In the first six months of this project, we have thoroughly analyzed our original inspiration for this research, which was thermoacoustic separation of hydrogen and oxygen from thermally dissociated steam near 2600 Kelvin. We attempted a complete design of what might become a practical apparatus, to motivate our basic research by making note of the relevant gaps in our scientific and engineering knowledge. We concluded that this original inspiration is too challenging to be credible, and shifted our focus to the sulfur-iodine cycle. We began revising our general-purpose, publicly available thermoacoustics code DeltaE to incorporate mixture-separation effects.

Program Impact:
This is a new project.

Interactions:
Penn State University; Sierra Lobo Inc.

Recognitions, Honors and Awards (at least in some part attributable to support under this program):

Personnel Commitments for FY2006 to Nearest +/- 10%:
Staff member G.W. Swift (25%), staff member D.A. Geller (0%), undergraduate J.P. Clark (40%)

Authorized Budget (BA) for FY04, FY05, FY2006:
FY04 BA $0 **FY05 BA $**0 **FY06 BA $**125,000

Laboratory Name: Los Alamos National Laboratory
B&R Code: KC020203

FWP and/or subtask Title under FWP:
Accelerated Molecular Dynamics Methods

FWP Number:
SCPE420

Program Scope:
The goals of this program are to develop methods for extending the time scale of molecular dynamics simulations to reach times relevant for diffusive processes and experiments; to improve the methods to make them applicable to the widest possible range of processes in chemistry, physics, materials science, nanotechnology, and biology; to apply the methods to problems of interest to LANL and DOE; and to collaborate with groups around the world to apply the methods to key problems in which they are expert.

Major Program Achievements (over duration of support):
Developed the parallel-replica dynamics method, which achieves parallel speedup for infrequent-event systems while maintaining exact dynamics. Developed the temperature accelerated dynamics (TAD) method, which achieves significant boost (many orders of magnitude) when barriers are high relative to the temperature. Used MD+TAD to simulate vapor-deposited metallic crystal and film growth at experimental deposition rates (seconds per monolayer), observing importance of highly concerted activated processes for surface smoothing even at low temperatures. Studied interstitial diffusion of H2 in fcc fullerene lattice, discovering unexpected multiple-occupancy mechanism. Performed first study of low-energy radiation damage and annealing on experimental time scales (seconds) with full atomistic detail (MgO). Developed modified parallel-replica dynamics method for driven systems.

Program impact:
The accelerated molecular dynamics concept, that the best way to evolve a system from state to state is to let the trajectory find its own way out of each state, is impacting the way people view infrequent-event systems and activated processes. Accelerated molecular dynamics simulations are elucidating key mechanisms in processes such as surface diffusion, vapor-deposited crystal growth, bulk diffusion, radiation damage annealing, carbon nanotube dynamics, grain boundary shear, metallic void growth/transformation, and nanocluster dynamics.

Interactions:
LANL internal: ASCI Enhanced Surveillance program; Advanced Fuels (AFCI) program; BES ceramics radiation damage simulation program; DOE/OS SCIDAC program on stress corrosion cracking; LDRD program on extended length-scale accelerated dynamics. *External*: Jacques Amar (University of Toledo), Luciano Colombo (University of Cagliari, Italy), Jimme D. Doll (Brown), Riccardo Ferrando (University of Genova), John Harding (Universiy College London, UK), Robin Grimes (Imperial College, London), John Hamilton (Sandia National Laboratory, California), Graeme Henkelman (Texas), Hannes Jonsson (University of Iceland), Janna Maranas (Penn State), Yuri Mishin (George Mason U.), Francesco Montalenti (University of Milano/Bicocca, Italy), David Sholl (Carnegie Mellon), Roger Smith (University of Loughborough, UK), James Sprague (Naval Research Laboratory), David Srolovitz (Princeton), Steve Stuart (Clemson), Greg Voth (Utah), John Wilkins (Ohio State), Wolfgang Windl (Ohio State).

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):
A.F. Voter (PI): Los Alamos Laboratory Fellow (2003), Fellow of American Physical Society (2006)
Nominated to editorial boards of Journal of Chemical Physics and Theoretical Chemistry Accounts
Numerous invited talks at national and international conferences (e.g., ACS, APS, MRS, TMS, AIChE, E-MRS)

Personnel Commitments for FY2006 to Nearest +/- 10%:
A.F. Voter 70%; Postdocs and collaborators funded from other sources

Authorized Budget (BA) for FY04, FY05, FY06:

FY04 BA $ 360,000	**FY05 BA $ 340,000**	**FY06 BA $ 310,000**

Laboratory Name: LANL
B&R Code: KC 0202030

FWP and possible subtask under FWP:
Integrated Modeling of Novel Materials

FWP Number:
SCPE420

Program Scope:
We have focused the theory effort to study short time and length scales with respect to the static and dynamic properties of materials. We address features observed by state of the art probes of matter such as scanning tunneling microscopes (STM), time-resolved scanning tunneling microscopes, near field scanning optical microscopes (NSOM), and other local and fast probes will be developed and used. This work involves an attempt to understand the dynamical properties of local structures that are measured by these novel probes, and how to exploit their unique functionalities. This work includes study of local electronic properties of strongly correlated materials and artificially created nanostructures, such as quantum dots, metal nanoparticles on DNA, impurity and vibronic states, Inelastic Electron Tunneling Spectroscopy (IETS), fast optical response of these materials, and electron-phonon coupled systems such as multiferroics. We will further develop basic theoretical methods that will make possible detailed analysis and predictions about specific experimental properties.

Major Program Achievements (over duration of support):
Developed a microscopic theory of the STM detection of the bosonic collective modes in high-Tc materials. Developed a description of the dynamics of a dislocation glass as a possible explanation of supersolid behavior in 4He. Developed a microscopic description of the coupling between atomistic lattice distortions and the electronic properties of unconventional superconductors. Explained coupled charge-spin dynamics in multiferroic hexaferrites. Developed a theory of molecular electronic states in organic/inorganic hybrid structures.

Program impact:
Applied advanced modeling and simulation tools to interpret and guide modern experimental probes of multiple spatial and temporal scales, including high magnetic fields, ultrafast time-resolved optical and vibrational spectroscopies, and scanning-tunneling microscopies.

Interactions:
Internal: J.D. Thompson, E. Bauer, T. Park (MPA-10) – heavy fermion Ce115 compounds, T Taylor, R. Averitt, R. Prasanumar(MPA-CINT), S. Crooker (NHMFL) – optics, S. Tretiak (T-12) – molecular electronics, Q. Jia(MST-STC) – multiferroics.
Several external collaborators: J.C. Davis (Cornell), E. Abrahams(Rutgers), T. Egami (Oak Ridge), P. C. Hammel (Ohio State), P. Littlewood (Cambridge), Allan H. MacDonald (UT Austin), Q. Si (Rice), L. Ku(Texas), J. Bonca and J. Demsar (Ljubliana).

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):
A.V. Balatsky- LANL Lab Fellow, Oct 2005. International advisory committee, Spectroscopies of Novel Superconductors, 2005, 2007. APS March meeting 2007, Invited Talk;

Personnel Commitments for FY2006 to Nearest +/- 10%:
A.V. Balatsky – 25%
S.Trugman – 25%
Authorized Budget (BA) for FY04, FY05, FY06 :
FY04 BA $ 170,000 **FY05 BA $ 150,000** **FY06 BA $ 130,000**

Laboratory Name: Los Alamos National Laboratory
B&R Code: KC0203010

FWP and possible subtask under FWP:
Molecularly Engineered Biomimetic Nanoassemblies

FWP Number:
SCPE951

Program Scope:
The program aims to develop an increased understanding of fundamental interactions that govern complex molecular and biomolecular assemblies, and to explore how structure, dynamics and function are linked in such assemblies. Areas of emphasis include the development of bio-inspired assemblies with energy transduction functions, control of optical or electronic responses in complex assemblies, and exploration of the role of dynamics in controlling assembly structures and functions. The approach used includes a combination of materials synthesis and fabrication, static and time-resolved spectroscopic characterization, optical and scanning probe microscopies, neutron reflectivity, and theory and modeling of electronic responses and assembly structures.

Major Program Achievements (over duration of support):
Studied Langmuir-Blodgett assemblies of conjugated amphiphilic molecules that mediate photo-induced charge transfer between layers of conjugated polymers and LB-deposited amphiphilic fullerene derivatives, and of photoconductive thin films based on assembly of amphiphilic quaterthiophene derivatives. Studied the electronic and optical properties of amphiphilic organic and organometallic oligomers of conjugated phenylene acetylene compounds. Created patterned hybrid and supported phospholipid bilayers, and characterized lateral mobility and the effects of spatial confinement within such structures. Demonstrated that phospholipid bilayers and monolayers can be formed on electronically active surfaces such as fullerenes and chemically modified fullerenes, and that the resulting assemblies can be characterized using optical spectroscopy, microscopy, ellipsometry, and neutron reflectivity. Demonstrated the use of protein recognition strategies to assist in the formation of controlled multi-layer assemblies of phospholipids, and carried out characterization studies using neutron reflectivity, ellipsometry, and atomic force microscopy. Modulated the luminescence properties of water-soluble conjugated polymers through the use of polyelectrolyte interactions in complex solutions, characterized the polymer's luminescent behavior using static and time-resolved spectroscopy and density-based material separation techniques, and developed a model that describes how heterogeneous assemblies in solution contribute to the overall luminescent behavior. Synthesized a lipidic affinity peptide for fullerenes and selected peptides from a combinatorial peptide library that bind to a specific conjugated polymer, enabling bio-inspired routes for assembly formation. Used Raman spectroscopy of surfactant-solubilized carbon nanotubes to provide the first quantitative determination of exciton-phonon coupling strengths. Demonstrated the development of substrate-supported phospholipid membrane assemblies containing ion channels on active substrates that allow for optical measurement of the channel's ionic transport functions.

Program impact:
The program has generated improved understanding of how to control complex self assembly to create functional nanoscale materials. Applications of such materials are found in energy production and storage, catalysis, and sensor technologies.

Interactions:
Atul N. Parikh (U.C. Davis); James A. Brozik (University of New Mexico); Darryl Sasaki (Sandia National Laboratories); Jarek Majewski (LANSCE)

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):
Organizer for Developing Nano-Bio Interfaces Symposium, MRS 2005 meeting (A. Shreve, 2005); Invited presentations by key personnel (Shreve, Parikh, Wang, Tretiak) at major national and international meetings.

Personnel Commitments for FY2006 to Nearest +/- 10%:
A. Shreve (20%); R. Rocha (30%); J. Martinez (10%); Y. Gao (postdoc, 100%); C. Wang (postdoc, 40%); H.-L. Wang (10%); S. Tretiak (20%); S. Iyer (10%).

Authorized Budget (BA) for FY04, FY05, FY06:
FY04 BA $ 645,000 **FY05 BA** $ 750,000 **FY06 BA** $ 600,000

Laboratory Name: Los Alamos National Laboratory
B&R Code: KC0203010

FWP and possible subtask under FWP:
Cooperative Phenomena in Molecular Nanocomposites.

FWP Number:
SCPE896

Program Scope:
The goal of this program is to create and study hybrid organic/inorganic materials in which cooperative self-assembly processes influence the formation and structure of the materials. This work includes the preparation of nanocomposite frameworks that are compatible with active biomolecular components, as determined by their structural integrity. Expertise in sample preparation and characterization is applied in an integrated manner to develop new insight into the balance between forces that govern the organization and responses of the materials studied. The program is performed collaboratively with researchers at Sandia National Laboratories.

Major Program Achievements (over duration of support):
Spectroscopic characterization of surfactant/silica mesophase nanocomposite films under controlled uv-light exposure. Masked deep-uv exposure has been used to remove the organic phase in self-assembled systems and organic/inorganic nanocomposite materials to generate patterned structure and organization in thin films as characterized by X-ray diffraction and various spectroscopic measurements. Developed methods for preparation and characterization of ordered nanocomposite silica films that can capture and spatially orient active proteins. Preparation of inorganic nanocomposite and nanoporous materials that contain molecular and macromolecular components to determine the effects incorporation of these components has on overall structure and assembly of nanostructured materials. Studied how nanostructure can affect the use of patterned nanocomposite materials for surface assisted mass spectrometry measurements.

Program impact:
This project has resulted in work published in high impact journals, such as *Nano letters*, *J. Phys. Chem. B*, and *Expert Reviews in Proteomics*. Developed a detailed understanding of organic template removal processes from organic/inorganic nanocomposite materials using photolytic methods. Development of spatially patterned biological/inorganic composite thin-film materials demonstrating increased stability and robustness of the biological components. Demonstrated that nanostructured materials deposited on silicon may be used to promote ionization/characterization of molecular compounds via a surface assisted mass spectrometry measurement.

Interactions:
Atul N. Parikh (U.C. Davis)
Alan Burns, Darryl Sasaki, Bruce Bunker (Sandia National Laboratories, Albuquerque)
C. Jeffrey Brinker (Sandia National Laboratories, Albuquerque and the University of New Mexico)
Frank V. Bright (University of Buffalo)
Gary A. Baker (Oak Ridge National Laboratory)

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):
Symposium Organizer for Developing Nano-Bio Interfaces, Materials Research Society Spring 2005 meeting (A. Shreve, 2005)

Personnel Commitments for FY2006 to Nearest +/- 10%:
A. Shreve (10%)
A. Dattelbaum (10%)

Authorized Budget (BA) for FY04, FY05, FY06:
FY04 BA $ 283,000 **FY05 BA** $ 85,000 **FY06 BA** $ 80,000

Laboratory Name: LANL
B&R Code: KC0203010

FWP and possible subtask under FWP:
Fundamentals of Hydroxide Conducting Systems for Fuel Cells and Electrolyzers
FWP Number:
SCPE974
Program Scope:

The vision of a Hydrogen Economy is compelling for reasons of improved energy security and environmental impact; however, before such a vision can be met there are major technological barriers that must be overcome. Namely, commercially viable technologies for the production (electrolyzers) and the use (fuel cells) of hydrogen must be developed. Hydroxide conducting systems can be used for either production or use of hydrogen and offer specific advantages compared to competing technology. To date investigation of hydroxide conductors for fuel cells or electrolyzers has been limited due to perceived limitations of durability, conductivity and/or carbonate formation. These areas have received limited study and to date little is known about the mechanisms or rates of the different decay processes. Our program combines experts in the area of fuel cells, synthetic chemistry and modeling to elucidate these decay mechanisms and design new chemical structures to overcome them. Our focus is on fully characterizing cationic materials (including currently employed potassium (which cannot be covalently bonded to a polymer) and tetraalkyl ammonium (which is known to degrade in contact with hydroxide)) and developing advanced cations capable of being covalently tethered and having sufficient stability and conductivity for use in electrolysis or fuel cell applications. The overall goal of the project is to provide an understanding of the fundamental processes that are important for the conductivity and durability of these materials. Physical processes of particular interest include: ion structure, ion charge distribution, interaction with water and anions, and the role of hydroxide versus carbonate.

Major Program Achievements (over duration of support):

Decay mechanisms of cations (including ammonium, sulfonium and phosphazenium) due to base attack have been identified under conditions relevant to fuel cells or electrolysis (1M hydroxide, 80C) and accelerated conditions (in contact with $KN(SiMe_3)_2$ in DMSO, or in contact with base at low water content). While membranes based on the standard tetraalkyl ammonium cations show poor stability at even 60C, these cations show reasonable stability to temperatures as high as 90C at sufficiently high water contents. The degradation of cations accelerates dramatically at low water contents (~5 waters per cation). The ability of water to stabilize cations to hydroxide attack has also been explored using molecular scale modeling. SN2 and ylide based decomposition routes have shown nearly equal activation barriers, and hydration studies of cations suggest water shields the cation from hydroxide in qualitative agreement with our chemical degradation studies. Molecular scale modeling has been able to match structures from neutron scattering experiments on tetramethyl ammonium hydroxide pentahydride crystals. These studies show that 25-35 water molecules are necessary for complete salvation shell of this cation. Because membranes swell only to a given water content (a typical number being 20 water molecules per ion), the lack of water in proximity to cation groups may play a major role in these materials stability. The dependence of stability of these materials on water content is an area of further study.

Program impact:

The work has lead to the PI being approached by the Army Research Office (ARO) to hold a Workshop on the topic. The final product of this Workshop is a report that ARO hopes to use as a funding guide for R&D in this area.

Interactions:
Organized ARO sponsored Workshop, involving ~65 international attendees on Alkaline Membrane Fuel Cells. The program involves Electrochemical, Chemistry and Quantum Chemistry Groups at LANL.

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):
3 Invited talks at the Alkaline Membrane Fuel Cell Workshop held December 11-13, 2006, Phoenix, AZ.
Invited review article to Physical Chemistry Chemical Physics on the project topic.

Personnel Commitments for FY2006 to Nearest +/- 10%:
Bryan Pivovar: 20%; Shaji Chempath: 100%; Lawrence Pratt: 20%; James Boncella: 20%; Brian Einsla: 100%

Authorized Budget (BA) for FY04, FY05, FY06:
FY04 BA $ 0 **FY05 BA $ 400,000** **FY06 BA $ 400,000**